

First Demonstration of Surface Passivation in Dye-Sensitized TiO₂ Solar Cells by an Additive in the Electrolyte

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ABSTRACT

The composition of the electrolyte is known to greatly influence the performance of dye-sensitized solar cells. It has been speculated that some components of the electrolyte passivate the TiO₂ surface against recombination; however, this has never been confirmed experimentally. We hereby present the first case of passivation of the TiO₂ surface against recombination by an additive in the electrolyte. Even though the additive also causes a downward movement of the TiO₂ bands, suppression of recombination prevails and an overall improvement in open-circuit photovoltage is observed. This work was conducted in collaboration with the DOE Office of Science program.

1. Objectives

Dye-sensitized photoelectrochemical cells are an attractive low-cost alternative to traditional solid-state solar photovoltaic devices [1]. In these cells, light-harvesting is achieved by a dye molecule chemisorbed on a porous, nanocrystalline TiO₂ film. The pores of this film are filled with an electrolyte, which reduces the oxidized dye back to its neutral state after photoinduced electron injection from the dye into the TiO₂. The electron percolates through the film until it reaches the conducting glass substrate or until it recombines with oxidizing species in the electrolyte. The interaction of ions in the electrolyte with the surface of TiO₂ can affect the solar cell performance in two principal ways. First, it can alter the recombination kinetics of photoinduced electrons with the redox couple. Second, it can cause charging of the surface, which will lead to movement of the TiO₂ bands with respect to the electrochemical potential of the redox couple. Both effects will result in changing the open-circuit voltage (V_{oc}) of the cell. For example, addition of a base to the electrolyte deprotonates the TiO₂ surface, causing an upward movement of the bands and a corresponding improvement in V_{oc} [2]. However, all additives studied to date have been shown to enhance photocarrier recombination [2].

In this report, we present the first example of an additive in the electrolyte that passivates the TiO₂ surface and suppresses recombination. The additive is also shown to cause the TiO₂ conduction band to move down. Overall, an improvement of the open-circuit voltage is observed.

2. Technical Approach

2.1 Sample preparation. Colloidal TiO₂ nanoparticles were prepared as described elsewhere [3]. The TiO₂ paste was spread on top of a conducting glass plate (F:SnO₂ glass) and

sintered to 450°C for 45 min. Typical film thickness and porosity was 10 nm and 60%, respectively. The films were sensitized overnight in a 5 × 10⁻⁴ M N719 dye solution in ethanol. Conducting glass (F:SnO₂) covered with a transparent Pt catalyst was used as the counter electrode. After sealing the cell, the electrolyte was inserted by predrilled holes in the counter electrode that were subsequently sealed, as well. The electrolyte was composed of 0.6 M 1-butyl-3-methylimidazolium iodide BMII, 0.03 M iodine in acetonitrile. The additive studied here is the guanidinium cation, shown in Fig. 1, included in the electrolyte in the form of guanidinium thiocyanate. Also, *tert*-butyl pyridine (TBP) was used as an additive for comparison with previous studies [2].

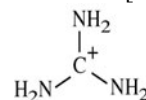


Fig. 1. Guanidinium ion

2.2 Transient photovoltage measurements. Recombination times were measured with the transient photovoltage technique [4]. The sample was illuminated with steady-state bias light at 680 nm at open circuit. A short (duration ~3 ns) laser pulse at 540 nm created a small extra density of photocarriers. The characteristic time of the exponential decay of the photovoltage to the steady-state value after the end of the laser pulse is equal to the recombination lifetime of photocarriers at that bias light intensity [4]. At a certain bias light intensity, the photoinduced charge at open circuit is estimated as the product of the recombination time and the short-circuit current density.

3. Results and Accomplishments

Under the assumption that there is negligible recombination at short circuit [5], the injection current from the dye into the TiO₂ equals the short-circuit photocurrent. At open circuit, the injection current from the dye equals the recombination current. Therefore, the short-circuit current density represents the recombination current density at open circuit, which is proportional to the recombination rate. The photoinduced charge density at open-circuit versus short-circuit current density for various additives in the electrolyte is shown in Fig. 2. Addition of TBP increases the recombination rate at a constant photoinduced charge density, in accordance with previous reports [2]. Interestingly, addition of guanidinium decreases the recombination rate by about an order of magnitude. When both additives are used, as is typically the case in a high-

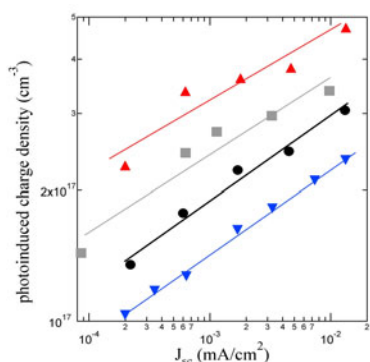


Fig. 2. Photoinduced charge density at open-circuit versus short-circuit photocurrent density for various electrolytes: without additives (●); with additives: TBP (▼), guanidinium (▲), guanidinium+TBP (■).

efficiency dye-sensitized solar cell, a net decrease in recombination rate by a factor of 4 is observed.

This is the first observation of the passivation of recombination in liquid-junction dye-sensitized TiO₂ cells by an additive in the electrolyte. Measuring the photoinduced charge in TiO₂ by a different technique, based on photoinduced near-infrared absorption [6], verified the above observation.

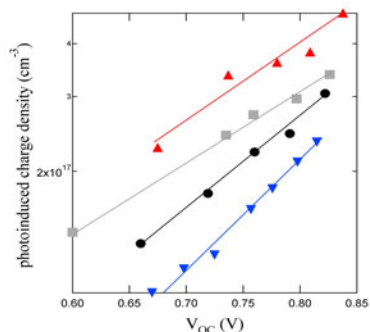


Fig. 3. Photoinduced charge density at open-circuit versus open-circuit photovoltage for various electrolytes: without additives (●); with additives: TBP (▼), guanidinium (▲), guanidinium+TBP (■).

To investigate band-edge movement caused by the interaction between additives and the TiO₂ surface, one needs to plot the photoinduced charge density at open circuit versus V_{oc} , shown in Fig. 3. TBP increased the open-circuit voltage at a constant charge density, indicating an upward movement of the TiO₂ bands, in agreement with previous reports [2]. On the other hand, guanidinium decreased the photovoltage at a constant photoinduced charge density, which is consistent with positive charging of the surface of TiO₂. The net effect of both additives is a downward movement of the bands and a corresponding small decrease in V_{oc} at constant photoinduced charge density.

The interaction of guanidinium with the TiO₂ surface is currently under investigation. It is speculated that the carbon of guanidinium binds to an oxygen on the TiO₂ surface. This scheme is consistent with positive charging of the surface, which leads to downward band-edge movement, as shown in Fig. 3.

The overall effect of surface passivation and band-edge movement is shown in Fig. 4. Improvement of V_{oc} by TBP due to band-edge movement is cancelled by the increased recombination. However, the passivation against recombination caused by guanidinium is more significant than the downward band-edge movement, and an overall improvement in V_{oc} is observed. The collective effect of both additives is also an increase in V_{oc} , which is primarily due to passivation of recombination by guanidinium.

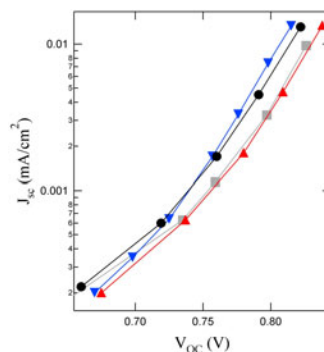


Fig. 4. Short-circuit current density versus open-circuit voltage for various electrolytes: without additives (●); with additives: TBP (▼), guanidinium (▲), guanidinium+TBP (■).

4. Conclusions

We demonstrate the first experimental evidence for passivation of the TiO₂ surface against recombination by an additive in the electrolyte of dye-sensitized solar cells. We find that the additive also causes a downward movement of the TiO₂ bands. The overall effect of this additive is to improve the open-circuit voltage of the cell.

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